

Modelling Multi Quantum Well Solar Cell Efficiency

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ABSTRACT: The spectral response of quantum well solar cells (QWSCs) is well understood. We describe work on QWSC dark current theory which combined with SR theory yields a system efficiency. A methodology published for single quantum well (SQW) systems is extended to MQW systems in the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $\text{InGa}_{0.53x}\text{As}_x\text{P}$ systems. The materials considered are dominated by Shockley-Read-Hall (SRH) recombination. The SRH formalism expresses the dark current in terms of carrier recombination through mid-gap traps. The SRH recombination rate depends on the electron and hole densities of states (DOS) in the barriers and wells, which are well known, and of carrier non-radiative lifetimes. These material quality dependent lifetimes are extracted from analysis of suitable bulk control samples. Consistency over a range of AlGaAs controls and QWSCs is examined, and the model is applied to QWSCs in InGaAsP on InP substrates. We find that the dark currents of MQW systems require a reduction of the quasi Fermi level separation between carrier populations in the wells relative to barrier material, in line with previous studies. Consequences for QWSCs are considered suggesting a high efficiency potential.

Key words: Quantum wells - 1: Solar Cell Efficiencies - 2: Modelling - 3

1 Introduction

The QWSC [1] is a p-i-n structure with narrow regions or quantum wells (QWs) of lower bandgap sandwiched between barrier layers with higher bandgap. Both are situated in the i region and subject to a field in the operating regime. The wells are narrow enough that carriers generated in them can only occupy discrete energy levels.

The control structures discussed here are p-i-n devices of similar material composition and dimensions as the QWSCs but with the QWs replaced with bulk material of the same composition as the barriers for barrier controls, or the barriers replaced with well material for well controls. In some cases $\text{InGa}_{0.53x}\text{As}_x\text{P}$ p-i-n heterostructures where the i region is made of material with either the confined well or the barrier bandgap are used as controls.

Experiment has shown ([2], [3]) that light absorbed in the QWs is converted to photocurrent with essentially unit efficiency, indicating good photogenerated carrier escape and collection efficiency.

Work on the efficiency of this system has raised a number of questions. It has been suggested [4] that the cell can be no more efficient than a homostructure with an equivalent bandgap in the ideal limit and that the V_{oc} is determined by the lowest bandgap in the cell. In real structures however further work ([5], [6], [7]) has indicated that assumptions regarding a constant quasi-Fermi level separation ΔE_f in the i region may not be true, in which case higher efficiencies are possible with this system.

This work investigates a QWSC dark current model dominated by Shockley-Read-Hall (SRH) recombination [8] in a number of QWSCs and control cells without wells in two different material systems with a view to exploring the efficiency of this system.

2 Model

2.1 Photocurrent

The modelling of the spectral response (SR) has been discussed previously [2] but is summarised here. It proceeds via solutions to the transport equations

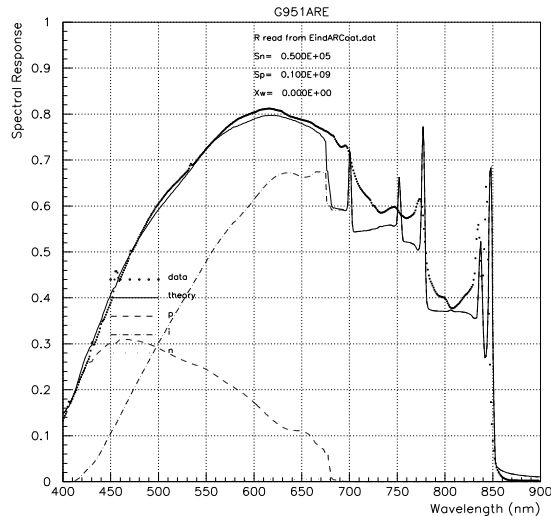


Fig. 1. Theory and experiment for a 50 well $\text{Al}_{0.36}\text{Ga}_{0.64}\text{As}$ QWSC with GaAs wells

for minority carriers in the charge neutral regions of the cell. Firstly these require information on minority carrier generation. The bulk absorption coefficient is expressed via a non linear interpolation between published data sets and determines the generation rate. The photocurrent from p and n regions is found by solving carrier current and continuity equations subject to minority carrier transport constants drawn from the literature. The surface recombination velocity and minority carrier diffusion lengths are the device dependent fitting parameters. The surface recombination velocity can be extracted from the short wavelength response, and the diffusion length from the broad shape of the spectral response for the p or n contribution as appropriate.

The intrinsic region calculation assumes 100% collection for carriers generated within it, which matches observation closely. For contributions from the well, the above barrier bandgap contribution is given by the absorption of the quantum well material in the bulk.

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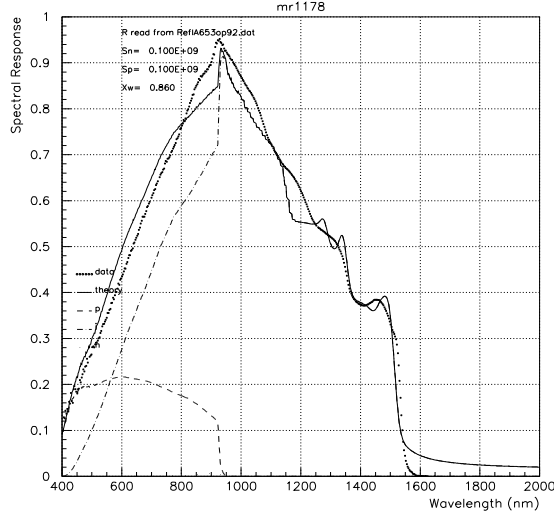


Fig. 2. Theory and experiment for a 30 well InGaAsP QWSC with InGaAs wells

Below the barrier bandgap for the quantum well levels, the absorption is calculated from first principles assuming infinite barrier thickness and using published values of well and barrier bandgaps in the bulk, and electron and hole effective masses by solution of the Schrödinger equation in the effective mass and envelope function approximations, and excitonic states are included [3].

SR theory and data for a 50 well GaAs/AlGaAs QWSC and a 30 well InGaAsP on an InP substrate are shown in figures 1 and 2 respectively. The approximations hold satisfactorily though increasing underestimation is visible near the top of the well in the region of transition from 2D to a 3D density of states (DOS). Overall the good fits show that the quantum well DOS is well described and that the assumption of unit escape efficiency for carrier escape from the wells is accurate.

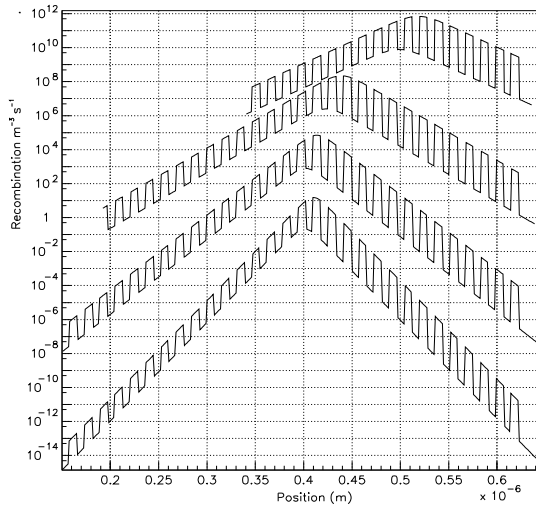


Fig. 3. Shockley-Read-Hall recombination profile at low to high bias for a thirty well QWSC showing enhanced recombination in the wells and reduced depletion at higher biases

2.2 Dark current

The dark current formulation used here expresses the dark current as a sum of ideal and SRH contributions. The ideal diode contribution is determined by charge transport in the neutral n and p regions which is determined by fitting the spectral response of these layers. We will see that this ideal contribution is negligible except at high forward bias in some samples.

As described in more detail in ref. [9], the SRH contribution to the dark current is the integral of the SRH recombination rate across the intrinsic region where it is non negligible because of significant populations of both electrons and holes. This method is applicable to MQW systems because the large number of wells removes the sensitivity of the dark current to well position, as opposed to the SQW case. The SRH rate for quantum wells can be expressed [10] in terms of the well understood quantum well DOS.

The SRH rate depends on the cell dimensions and material which are well known from the epitaxial growth. Given the knowledge of the DOS this leaves the hole and electron lifetimes in the intrinsic regions as free parameters in the absence of direct measurement. If electron and hole lifetimes are made significantly different in the material being considered (well or barrier), the slope of the dark current on a log-linear scale (the ideality) changes significantly in contradiction with experiment.

This leaves as two parameters the carrier lifetimes in the barriers, and in the wells. These two values are determined by fitting the dark currents of control structures made of material equivalent to wells and barriers respectively where they are the sole free parameters.

Given this determination of carrier non radiative lifetimes and the knowledge of the DOS, this leaves no free parameters in fitting the dark currents of QWSC structures, as will be seen subsequently.

A further assumption we examine is that the Quasi-Fermi level separation ΔE_f is constant across the i region and determined by the applied bias. Reducing ΔE_f implies lower carrier concentrations and hence lower recombination in the wells as investigated below.

Figure 3 shows a calculated SRH recombination rate in a 30 well GaAs/Al_xGa_{1-x}As QWSC with x=36%. The four curves correspond to applied biases ranging from near zero to just below the build-in voltage, for the depleted or field bearing section of the intrinsic region. The depletion width is reduced as the applied bias is increased due to the fixed charge corresponding to unintentional background doping. This background doping is p type in this case, which is why the SRH peak shifts towards the n region on the right of the graph.

The recombination in the wells is about two orders greater than in the barriers in this case and asymmetric due to different p and n region effective densities of states. This profile corresponds to a dark current which fits the data in figure 6 well showing a reduced ΔE_f in SRH dominated material as discussed below.

3 Comparison with data

3.1 AlGaAs

Figure 4 shows theory and experiment for two GaAs p-i-n well controls of different dimensions from different growth runs to check repeatability. The ideal diode Shockley dark current component (dashed line) is negligible except at high bias where it starts to have an effect. The dark currents of the two cells are essentially identical within errors, but the model requires a slightly longer lifetime of 11ns in the wider cell versus 8ns in the narrower. Together the results from these different cells show a good consistency in model predictions and hence material reproducibility.

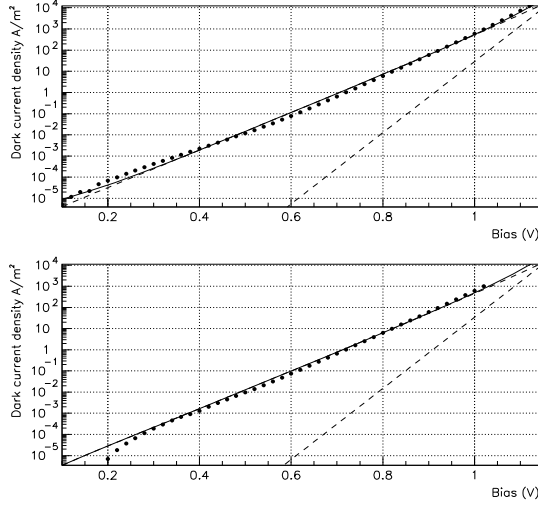


Fig. 4. Theory and experimental dark current for a GaAs MQW control with $1\mu\text{m}$ wide i region (upper figure) and $0.9\mu\text{m}$ wide i region giving non radiative lifetimes of 8ns and 11ns for undoped GaAs

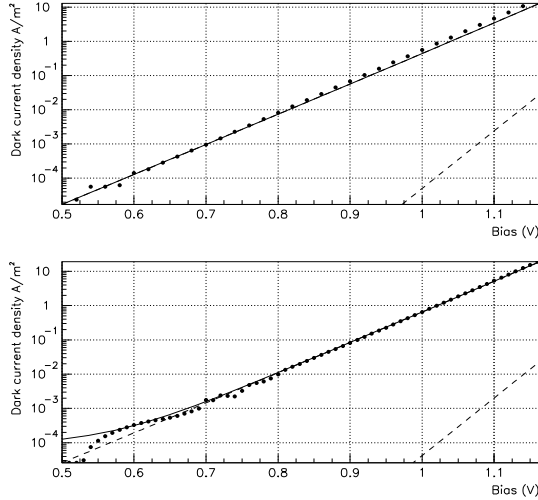


Fig. 5. Theory and experimental dark current for an AlGaAs MQW control with $0.48\mu\text{m}$ wide i region (upper figure) and SQW $0.31\mu\text{m}$ wide i region control giving non radiative lifetimes of 0.7ns and 0.3ns for undoped $\text{Al}_{0.36}\text{Ga}_{0.64}\text{As}$

Figure 5 shows similar results for two AlGaAs controls from different growth runs some time apart with the thicker MQW control i region 55% wider than the narrower SQW control cell. These controls are also consistent, and determine lifetimes of 0.7ns and 0.3ns in undoped $\text{Al}_{0.36}\text{Ga}_{0.64}\text{As}$. Again the ideal component is negligible in this case and lower due to different p and n layer characteristics.

The consistency of these values gives us confidence in applying these lifetimes to material in QWSCs. We use the MQW control lifetimes (8ns for GaAs and 0.7ns for AlGaAs). Two examples of modelling GaAs/ $\text{Al}_{1-x}\text{Ga}_x\text{As}$ QWSC structures are shown in figure 6. The QWSCs were again grown in different growth runs and in different institutions and have a significantly different structure. One features 50 wells and a i region

$0.81\mu\text{m}$ wide, the other 30 wells in $0.48\mu\text{m}$ i region.

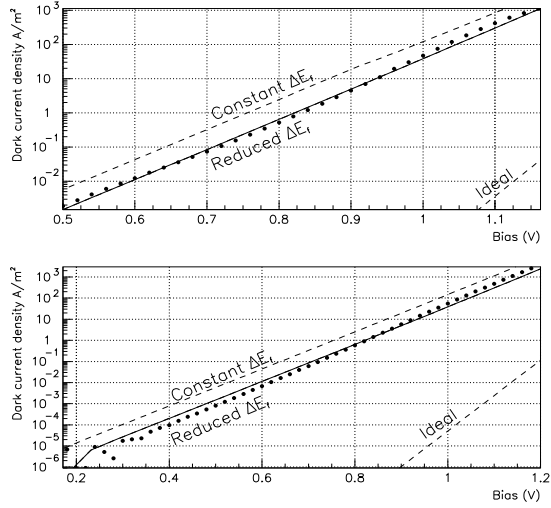


Fig. 6. Theory and experimental dark current for two AlGaAs QWSCs with different i region widths and number of wells, using the same ΔE_f in the wells

The two graphs show the methodology applied to the two samples, with a fit to the data (dots) assuming a constant ΔE_f (dashed line), and the same with a reduced ΔE_f which agrees closely with the data. The value of ΔE_f is 140meV in both cases.

This value is larger than the value reported in ref. [11] for SRH dominated SQW samples and developed in ref. [10]. A difference is not surprising given the different approaches and different MQW and SQW samples. Moreover, ref. [11] shows that the depletion approximation for SRH dominated material is good for biases up to the operating voltage, and is confirmed here since we reach the same conclusion with similar values in MQW and SQW samples. This is that the ΔE_f is reduced in QWSC structures, as demonstrated in SQWs.

For this cell the constant ΔE_f calculation predicts an AM1.5 efficiency 14% above what might be expected for this cell based on a constant ΔE_f , in agreement with experimental. The fact that this cell does not appear to follow the constant ΔE_f picture therefore yields a significant increase in efficiency in this system over what might be expected from the more simple prediction.

3.2 InGaAsP

Figure 7 shows the same analysis for the dark currents of QWSCs in $\text{InGa}_{0.53x}\text{As}_x\text{P}$ on InP substrates. The upper and lower curves are well and barrier controls, made of InGaAsP lattice matched to InP and are analogues of graphs 4 and 5.

The well control is a double heterostructure control with an i region made of material with the well effective bandgap including confinement. The barrier control is a double heterostructure control with an i region made of barrier material. In this case the bulk well control lifetime of 70ns is shorter than that of the barrier control which is 400ns, but the conclusions are the same.

The middle curves show modelling of the QWSC dark current with the lifetimes derived from the two controls. The dashed line again shows the expected dark current with a constant ΔE_f given by the applied bias.

The fit requires a reduction in ΔE_f level of 130meV in the well. The ideal component is again negligible.

This shows similar behaviour to the AlGaAs case with a slightly reduced ΔE_f consistent with the slightly shallower wells visible in the spectral response fits in figure 1 and 2. The sum of well depths in the GaAs/Al_xGa_{1-x}As case is approximately 400meV versus 290meV in the InGa_{0.53x}As_xP case including confinement. Furthermore, InGa_{0.53x}As_xP well have different hole to electron band offsets of 16% versus about 33% in GaAs/Al_xGa_{1-x}As with the valence well being deeper.

This shows similar conclusions in a second material despite significantly different band structures and carrier properties, and a narrower voltage range because of the lower built in voltage. Although there is uncertainty in the value of ΔE_f due to the theoretical approximations used, the reduction confirms the high efficiency potential of QWSCs.

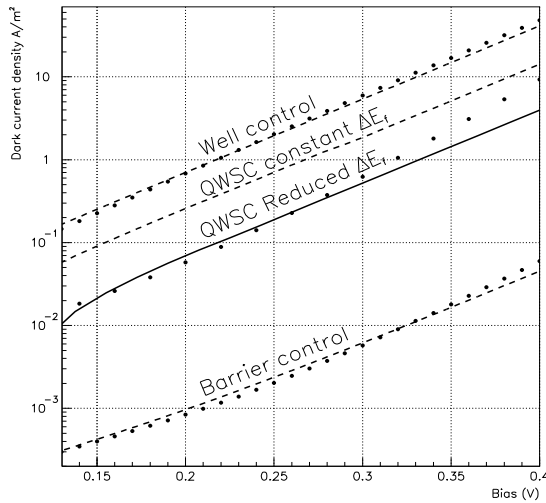


Fig. 7. Theory and experimental dark current for a InGa_{0.53x}As_xP MWQ (centre curves) and well and barrier controls showing a similar dark current reduction to GaAs/Al_xGa_{1-x}As QWSCs

4 Conclusions

The QWSC benefits from an increase in photogeneration in the wells but suffers from increased recombination in the lower bandgap well regions. In order to study which effect is greater we study photocurrent and dark current and express the modifications to dark and photocurrent in terms of the quantum well density of states. The photocurrent from the wells is determined with no free parameters to good accuracy.

The dark current for the control homojunctions is well understood. Modelling these gives us an estimate of carrier lifetimes in the depletion region, together with verifying the transport parameters used in the SR calculation at the onset of ideal diode behaviour, if present.

The QWSC dark current depends on four lifetimes. We reduce this to two by assuming that hole and electron non radiative lifetimes are equal. In the absence of direct measurements we derive the barrier lifetimes from controls with the barrier composition. Similarly, controls with the well composition set an upper limit on the well lifetimes employed.

A consistent set of lifetimes in two materials emerges despite differences in growth and device design which gives confidence in the lifetimes used.

We see a systematic overestimation of the dark current. This can be explained in terms of a smaller value of ΔE_f in the wells. This strongly suggests that these structures have the potential to be efficient solar cells.

The treatment used here does not apply to SQW structures because of the approximations made. For SQW samples the position of the quantum wells and the background doping are significant and require an exact solution satisfying Poisson's equation.

We note however that the treatment applies reliably to MQW systems studied here since dark current is determined mainly by the balance between QW and barrier material, in that on average the position of the wells is not critical. Furthermore the depletion approximation is reliable up to the operating voltage [11]. This is borne out by the range of control and QWSC GaAs/Al_xGa_{1-x}As and InGa_{0.53x}As_xP samples examined and comparison with previous exact solutions.

Finally we see consistently similar effects in two systems with very different materials parameters that can explain the higher efficiency observed in the QWSC system.

References

- [1] Barnham KWJ and Duggan G, *A New Approach to High Efficiency High-Bandgap Solar Cells*, J. Appl. Phys. **67** (7), 1990
- [2] M.Paxman, J.Nelson, K.W.J.Barnham, B.Braun, J.P.Connolly, C.Button, J.S.Roberts and C.T.Foxon *Modelling the Spectral Response of the Quantum Well Solar Cell* J.Appl.Phys. **74**, 614 (1993).
- [3] Jenny Nelson "Quantum-Well Structures for Photovoltaic Energy Conversion." Thin Films, Vol. 21, p. 311-368 (Academic Press, 1995)
- [4] G. L. Araujo et al., Proc. 12th European Photovoltaic Solar Energy Conference, pp. 1481-1484 (1994)
- [5] Keith Barnham, James Connolly, Paul Griffin, Guido Haarpaintner, Jenny Nelson, Alexander Zachariou, Jane Osborne *voltage enhancement in Quantum Well Solar Cells*, J. apply. Phys **80** 1201 (1996)
- [6] Jenny Nelson, Benjamin Kluitinger, Ernest S.M.Tsui, Keith Barnham et al., *Quasi-Fermi Level Separation in Quantum Well Solar Cells*, 13th European Photovoltaic Energy Conference, Nice, pp150 (1996)
- [7] E.S.M Tsui, J.Nelson, K.W.J. Barnham, C.Button and J.S.Roberts, *Determination of the Quasi Fermi level separation in single quantum well p-i-n diodes* J. Appl. Phys. **80** (7) (1996)
- [8] Shockley, W. T. Read, and r. N. Hall, Phys. Rev. Lett. **87**, 835 (1952)
- [9] James P. Connolly, Jenny Nelson, Keith W.J. Barnham, Ian Ballard, C. Roberts, J.S. Roberts, C.T.Foxon, *Simulating Multiple Quantum Well Solar Cells*, Proc. 28th IEEE Photovoltaic Specialists Conference, Anchorage, Alaska, USA, Sept. 2000, p. 1304-1307.
- [10] Jenny Nelson, Ian Ballard, Keith Barnham, James P. Connolly, *Effect of quantum well location on single quantum well p-i-n photodiode dark currents*, J. Appl. Phys. **86** (10), 1999
- [11] Jenny Nelson, Jenny Barnes, Nicholas Ekins-Daukes, Benjamin Kluitinger, Ernest Tsui and Keith barnham *Observation of suppressed radiative recombination in single quantum well p-i-n photodiodes* J.Appl.Phys. **82**, 6240 (1997).